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Beer-Lambert-Law Parametric Model of Reflectance Spectra for Dyed Fabrics

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14. ABSTRACT This study examines a parametric model of diffuse reflectance for the purpose of simulating the spectral response of near-infrared (NIR, 0.7-0.9µm) and shortwave infrared (SWIR, 0.9-1.7µm) absorbing dyes for military applications. This analysis establishes the ground-work for the development of a prediction tool, which when given the constituent materials available, will enable rapid optimization of NIR/SWIR band contrast matching of composite systems (e.g., uniforms and ancillary gear) for a given combat Area of Responsibility (AOR). The dyes considered for prototype analysis are triarylamine, tetraaryldiamine, transition metal dithiolene, and indolium iodide. Military camouflage fabric consisting of 50/50 nylon/cotton blend (NYCO) in a ripstop weave printed with four-color digital pattern was used as the test substrate for NIR dye application. The results of this study provide validation of the constructed parametric model within reasonable error, for practical applications including simulating NIR/SWIR spectral responses corresponding to fixed dye and dye blend concentrations in prototype camouflage fabrics.					
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Introduction

Visual augmentation systems (VAS) used for detection and identification of personnel targets on the battlefield have primarily utilized the visual (Vis, 380-700nm), NIR, midwave-infrared (MWIR, 3-5 μ m), and longwave-infrared (LWIR, 8-12 μ m) portions of the electromagnetic spectrum. Devices such as Gen 3 Extended Blue Night Vision (NV) devices have increased spectral response from the visual to NIR spectral range (0.35-1 μ m). Previous developments in camouflage treatments have therefore focused in this spectral region. One such treatment embodies various techniques for dyeing, printing, and embedding NIR reflective pigments in military fabrics. Experiments with NIR-absorbing dyes in fabric have demonstrated the ability to adjust the NIR reflectance of the material to match the spectral response of a specified AOR. However, certain dyes and dye concentrations have a tendency to darken the fabric, changing the reflectance characteristics in the visible spectrum. Another problem concerns the fact that certain NIR dye treatments fail to provide effective contrast matching in the SWIR spectrum.

Advances in detector technologies, e.g., Indium Gallium Arsenide, have enabled manufacture of SWIR cameras with enhanced sensitivity and smaller size, weight, and power (SWaP). The versatility of these detectors has increased the likelihood of SWIR devices proliferating across the battlefield. The addition of a new detection threat creates an optimization problem for camouflage designers that must continually adjust patterning and contrast matching to account for detection threats across multiple bands.

There exists a need to develop and apply a SWIR signature reduction treatment to existing and future military uniforms while maintaining acceptable visible and NIR signatures. One possible solution entails the development of a parameter space for process optimization of dyed fabrics. An optimization algorithm would use the parameter space to determine the optimum dye-fabric combination and fabrication process given a target reflectance spectrum and the constituent materials available. To reach the point of process optimization, various NIR and SWIR absorbing dyes, military fabrics, fabrication processes, and parametric reflectance models must be examined.

In the current framework, the formulation of a parametric model is based on an inverse analysis approach [1,2,3,4,5]. A constructed model can either be purely phenomenological or semi-phenomenological in nature. Semi-phenomenological models are formulated for parameter adjustment with respect to specified target measurements (i.e., measurements to be modeled), as well as inclusion of material properties obtained through inverse analysis of other spectral measurements.

Optimizing reflectance spectra of dyed fabrics with respect to given specifications poses the problem of optimizing diffuse reflectance materials. Diffuse reflection defines a separate regime for spectroscopic analysis of material surfaces and layers. The physical processes underlying diffuse reflectance are discussed extensively in references [6,7,8,9,10,11]. Spectral analyses using parametric models of diffuse reflectance have been applied successfully for identification and characterization of soil minerals and paper containing ink. Parametric models applied for these analyses include those based on multiple reflections from layered systems (i.e., scattering matrix formulations) [12,13,14], the Kubelka-Munk theory of diffuse reflectance (and formulations derived from it) [15,16,17,18], and exponential-function representations (formally similar to the Beer-Lambert Law) [8]. The parametric model of diffuse reflectance presented in

this study, which is for analysis and characterization of dyed fabrics, is based on the Beer-Lambert Law for extinction [19,20], and absorption coefficients that are obtained by inversion of transmission spectra for dyes in solution [21]. Accordingly, this parametric model is semi-phenomenological in that parameter adjustment is with respect to underlying processes, e.g., scattering, other than absorption.

An underlying condition for validity of the model considered in this study is transferability of absorption coefficients, obtained from transmission spectra for dyes in solution, to modeling the dielectric response of dyes within a solid composite material, comprising a dyed fabric. Strictly, the absorption coefficients obtained by such inverse analysis are to be interpreted as estimates of the dielectric response of individual dye molecules. This follows from studies of solvent effects on absorption spectra, which have shown that spectra of dissolved dyes depend on the nature of dye-solvent interactions. In particular, that wavelengths for maximum absorption, spectral shifts, and other spectral features depend on dye-solvent interactions [22,23,24]. These permittivity functions, however, should be considered as “reasonable” estimates of dielectric response. This follows from the general dependence of absorption spectra on dye-solvent interactions, which tends to preserve dominant spectral features, regardless of changes in intensity maxima, wavelengths for maximum absorption, and shape of absorption band (see reference [24] for example). Finally, it must be noted that, by inclusion of adjustable weight coefficients A_j defined below, the parametric model is structured for statistical variability with respect to extinction processes associated with dyed fabrics, which includes those depending on interactions of dye molecules with those comprising a fabric, as well as heterogeneous dye-molecule distributions within a fabric. Accordingly, the statistical nature of the parametric model, requires only reasonable estimates of dye absorption coefficients that preserve dominant spectral features. That is to say, with respect to the parametric model, absorption coefficients assume the role of deterministic constraints, rather than specified material properties.

Materials and Methods

Dyes. This study examined Triarylamine, tetraaryldiamine, transition metal dithiolene, and indolium iodide dyes supplied by Fabricolor Holding Int'l. Dyes were chosen for their unique absorption features in the NIR/SWIR bands and ease of sample preparation due to their solubility in common laboratory solvents. All four dyes have wavelengths of maximum absorption in either the NIR or SWIR bands, with appreciable spectral features extending into the visible spectrum. Table 1 contains the solvent and wavelength of maximum absorption associated with each dye.

Fabric. The base fabric considered for dye application was a military camouflage fabric consisting of 50/50 nylon/cotton blend (NYCO) in a ripstop²⁶ weave printed with a four-color, AOR1 desert digital pattern (Figure 1). The parametric model considered in this study assumes a rough surface, finite and non-uniform thickness, and a heterogeneous composition, which is based on AOR1 desert camouflage pattern design.

Dyed-Fabric Sample Preparation. For each dye and corresponding solvent, a stock solution of 30 g L⁻¹ was made. Serial dilutions of each stock solution were prepared, consisting of 3.0, 1.5, 0.3, 0.15 and 0.03 g L⁻¹. Twenty dye-solutions were prepared in total. One square yard of 50/50 NYCO Ripstop fabric was cut from the roll and placed under a Freeman Schwabe cutting press. A 2"x2" Fremont steel rule cutting die was used in combination with the mechanical press to make 20, 2"x2" fabric samples. Dye-fabric samples were prepared by pipetting 1 mL of each dye solution onto the center of each 2"x 2" fabric piece. The pipetting speed was adjusted as to avoid

pooling of the dye solution on the fabric surface. Dye-fabric samples were given 24 hours to dry before total reflectance measurements were made.

Spectral Measurements of Dyed-Fabric Sample. Measurements of total reflectance were made using a UV/Vis/NIR/SWIR spectrophotometer (Perkin-Elmer® Lambda™ 1050, Waltham, MA, USA) in combination with UV WinLab (V6.0.3, Perkin Elmer) software. Reflectance was measured from 250 nm to 2500 nm at 5 nm stepping increments. All measurements were 8 degree hemispherical in total reflectance collection mode. The Lambda 1050 incorporated a double beam, 150 mm integrating sphere housing a photomultiplier tube (PMT) detector for the UV-Vis (175 – 860 nm) region and an Indium Gallium Arsenide (InGaAs) detector for the NIR-SWIR (860 - 2500 nm) region. Radiation sources included a deuterium lamp for operation in the UV (175 – 319 nm) and a tungsten halogen lamp for use in the Vis-NIR-SWIR (319 – 3000 nm). A light source change at 319.2 nm and a detector change at 860.8 nm occurred automatically during monochromator slewing. For UV-Vis wavelengths, the slit width was fixed at 4 nm. For NIR-SWIR wavelengths, the slit width was set to “Servo” mode, which automatically adjusted the slit width during scanning to maintain constant energy at the detector. Aforementioned spectrophotometer settings were adopted according to those proposed by Fort Belvoir Night Vision Laboratory for purpose of comparative studies between agencies.

Parametric Model of NIR Reflectance Spectra for Dyed Fabrics

Physically consistent parametric models provide a means for investigating the dielectric response characteristics of a given system that is characterized by a given material, or combination of materials, and geometry, in terms of both inverse and direct analysis. The parameters defined by these models can be material properties (e.g., optical constants), phenomenological quantities and combinations of both [27,28,29]. For reflection from a dyed fabric of finite and nonuniform thickness, whose material composition is heterogeneous, it is plausible that a general framework for parametric modeling of reflectivity spectra for diffuse reflectance can be based on the Beer-Lambert law for extinction, i.e., attenuation of an electromagnetic wave, by scattering and absorption of radiant flux as it traverses a particulate medium [19]. A constructed parametric model that combines the Beer-Lambert law with other physical assumptions (described in what follows) is given by

$$R_{f+d}(\lambda) = R_f(\lambda) \exp(-\alpha_d \langle L \rangle) \quad (1)$$

where

$$\alpha_d \langle L \rangle = f(\lambda) = \sum_{j=1}^{N_j} A_j \alpha_j(\lambda) \quad (2)$$

and

$$Z_R = \sum_{n=1}^N w_n \left(R_{f+d,M}(\lambda_n) - R_m(\lambda_n) \right)^2 \quad (3)$$

where α_j is the absorption coefficient of component material j (see reference 4) and λ denotes wavelength dependent quantities. The formal procedure underlying inverse analysis based on

Eqs.(1)-(3) entails adjustment of the coefficients A_j of known absorption coefficients α_j . This approach defines an optimization procedure where the reflectivity spanning the range of wavelengths is adopted as the quantity to be optimized. Constraint conditions are imposed on the reflectivity by minimizing the objective functions defined by Eq. (3), where $R_m(\lambda_n)$ is the measured or target reflectivity for wavelength λ_n . The quantities w_n ($n=1, \dots, N$) are weight coefficients that specify relative levels of influence associated with constraint conditions $R_m(\lambda_n)$. The parametric model defined by Eqs.(1)-(3) consists of two types of parameters, which are dielectric response properties (i.e., absorption coefficients) and adjustable parameters representing the combined influence of other physical processes and system conditions. In addition, the linear combination defined by Eq.(2) assumes no interaction between component dyes within the fabric. Of course, for a single dye $f(\lambda)=A\alpha(\lambda)$.

The mathematical foundation of diffuse-reflectance spectral analysis based on Eqs.(1) and (2) is that of least-squares parameter optimization [30,31]. A significant aspect of least-squares parameter optimization is the choice of a sufficiently complete set of basis functions. This implies that all possible modes of a given process can be modeled parametrically by linear combinations of these functions. Accordingly, the parametric models defined by Eqs. (1) and (2) adopt absorption coefficients as basis functions. The general form of Eqs. (1) is based on trend features characteristic of reflectance spectra. Accordingly, the parametric model defined by Eqs.(1) and (2) is based on the Beer-Lambert extinction model of reflectance, whose general form is consistent with spectral features of diffuse reflectance. A derivation of Eq.(1) follows from the Beer-Lambert law for extinction, relating the transmitted to incident intensity I_T and I_0 , respectively, given by

$$I_T(z) = I_0 \exp[-\alpha_{ext}(\lambda)z] \quad (4a)$$

where

$$\alpha_{ext}(\lambda) = N(C_{abs} + C_{scat}) \quad (4b)$$

and N , C_{abs} , C_{scat} and z are the particle density, absorption and scattering cross sections, and depth of penetration, respectively, and the background-subtracted, or equivalently, background-normalized reflectance defined by the relation

$$R_d(\lambda) = \frac{R_{d+f}(\lambda)}{R_f(\lambda)} \quad (5)$$

where R_f , R_d and R_{f+d} are reflectances of the base fabric, pure dye and dyed fabric, respectively. A discussion of Eq.(4) and associated physical assumptions is given in reference [19]. Equation (5) follows from the assumption that the contribution to the reflectivity due to the fabric can be factored out from that of the combined system of dye and fabric. This relation follows from the Beer-Lambert law and formalism of the scattering-matrix [20]. In particular, the scattering matrix relates functionally the optical response of a given composite material to a finite depth of penetration L , or equivalently, to a finite number of layers of specified thicknesses, whose sum equals L . The scattering matrix describes both homogeneous and heterogeneous systems, which can be characterized by statistical ensembles making up the layered material [12,20]. The form of Eq. (2) represents an important aspect of the constructed parametric model. This follows in that the Beer-Lambert law is based on absorption and scattering coefficients, C_{abs} and C_{scat} , respectively, with respect to transmission through a finite thickness of particulate material (see

Eq. (4b)), and thus does not formally represent reflectance due to extinction resulting from both transmission and reflection as a function of depth of penetration. A derivation of the parametric model defined by Eqs. (1) and (2) is given in Appendix I.

The parametric model defined by Eqs. (1) and (2) adopts absorption coefficients for modeling reflectivity spectra of dyes in fabric. Absorption coefficients were previously determined by inverse analysis of transmission spectra corresponding to dyes in solution. In general, it should not be assumed that dielectric response properties associated with transmission through solutions are the same as those for transmission through solid composite systems. Accordingly, an important validation of the parametric model is that, for the dye-fabric systems considered, there is agreement between predicted and measured reflection and transmission spectra for dyes in fabric. In what follows, good agreement is obtained between modeled and measured reflectance spectra, based on adjustment of a single parameter (proportional to all other attenuation influences), and thus represents one type of validation of absorption coefficients for dyes in fabric. This agreement also shows consistency of the parameter model with scattering-matrix formalism, where reflectance and transmission may be decomposed into multiplicative component contributions [20]. Another type of validation of the absorption coefficients is that of good agreement between modeled and measured transmission spectra. For this purpose, a case study analysis is presented in Appendix II that compares predicted transmission spectra, obtained by inversion of dyes in solution, and measured background-subtracted transmission spectra for dyes in fabric, which shows small differences between these spectra. It should be noted that the results of this analysis imply weak coupling between intramolecular modes associated with absorption, and intermolecular modes of the host environment, either solvent molecules or dye-crystal structures within a fiber. This weak coupling does in turn imply that the reflectivity of combinations of dyes in fabrics can be predicted using relative-concentration-weighted sums of absorptions coefficients, i.e., Eq.(2).

Results and Discussion

A parametric model was examined to characterize the diffuse reflectance properties of dyed fabrics. The model was constructed using the Beer-Lambert Law Eq.(4) and background-subtracted reflectance defined by Eqs. (5). Consistent with the Beer-Lambert law, diffusely reflected radiation is related to changes in scattering, absorption, and thickness of a dyed fabric layer. The layer is assumed infinitely thick, leaving reflectance in terms of the relative proportions between absorption and scattering. With respect to the Beer-Lambert law, due to the complex nature of scattering, and the uncertainty with respect to dyed fabric microstructure, the combined influence of absorption and scattering are represented in part phenomenologically. Accordingly, the function $f(\lambda)$ defined by Eq.(2) represents the combined influence of absorption and all other underlying physical processes contributing to reflectance within the dyed fabric layer. For the purpose of parametric modeling, the function $f(\lambda)$ is expressed as a lumped parameter consisting of known absorption coefficients, α_j , intrinsic to each dye and parameters A_j (see Eq.(2)). The absorption coefficients α_j are determined previously through inverse analysis of transmission spectra for dyes in solution, and the coefficients A_j are adjustable parameters accounting for physical processes other than absorption, statistical variations in fabric thickness, dye distribution in fabric, and variations in concentration. That is to say, the absorption coefficients α_j are assumed to be a known material property, within reasonable estimates, in contrast to phenomenological parameters A_j .

Figures (2)-(5) show reflectance spectra of the four dyes under analysis as a function of dye concentration and wavelength. The reflectance spectrum of a control fabric containing no dye is shown in each figure for comparison. Each experimental spectrum was modeled by adjusting parameter A until the objective function (Eq. (3)) was minimized. Figures (6)-(9) show comparisons between modeled and experimental data for each dye concentration. The good consistency of these fits demonstrates the acceptable prediction accuracy of the parametric model for diffuse reflectance by the dyed fabrics considered. The results also show that the absorption coefficient for a dye, which has been determined by inverse analysis of transmission spectra for dyes in solvents [21], can be validated as reasonable estimates of the absorption coefficient for dyes in fabrics. Referring to Figures (6)-(9), one must interpret differences between modeled and experimental data with respect to the statistical character of reflectance from the dyed fabrics. In particular, because the background spectrum R_f is inherently an average quantity. Comparison of modeled and measured spectra should be within an adjustable scale factor. In principle, the objective function could be weighted to include optimal scaling with respect to R_f in Eq.(1). Shown in Figure 10 are values of A for each dye as a function of dye concentration, providing its determination for intermediate concentrations.

Figures 11 and 12 show comparisons of measured and modeled reflectance spectra for different relative concentrations of triaryllamine (Dyes 978) and indolium iodide (Dye 775) in solution prior to fabric dyeing. Indolium iodide was fixed at 0.3 g/L in Figure 11 and 0.15 g/L in Figure 12, while the concentrations of triaryllamine were varied arbitrarily. Again, these comparisons are within an adjustable scale factor associated with the inherent variability of the background reflectance R_f in Eq.(1). Referring to these figures, one can see that the dominant absorption signature associated with indolium iodide, centered around 775nm, remains clearly distinguishable with respect to that triaryllamine, centered around 978nm. Further, the agreement between modeled and measured spectra demonstrates that the reflectance spectra for combinations of dyes can be represented parametrically by a linear combination of absorption coefficients, Eq.(2), where influence associated with the relative concentration of dye molecules as well as the influence of processes other than absorption, e.g., scattering, can be represented by weight coefficients A_j .

Differences between model and experiment can arise from the physical characteristics of the dye fabric layer. Samples may have more heterogeneity than is consistent with underlying assumptions of the model. There may be partial reflection off the fabric surface, which is not considered by the model. In particular, how dye molecules are distributed within the fabric is unknown. At lower concentrations, the dielectric response of dye molecules is uncoupled from each other. As dye concentration increases, dye molecules may mutually interact due to decreased intermolecular separation. Further, it must be remembered that the distribution of dye molecules within the fiber, which depends on the dye-deposition process, and fabric microstructure are all statistical in nature. The statistical variation of these process parameters will affect the absorption, scattering, and diffuse reflectance of the samples. As a result, for a given set of dyed-fabric samples having the same dye concentration, the reflectance spectra can be different. Accordingly, the parametric model defined by Eqs.(1) and (2) should be applied to collections of samples that are sufficient for statistical analysis.

The characteristics of parameter adjustment with respect to a wide range of wavelengths was examined. Adjustment of parameter A had stronger influence on the shape of the modeled reflectance curve in the vicinity of absorption maxima. By achieving the best fit possible in this region, the model showed a tendency to underestimate the reflectance at longer wavelengths

(1250-2500 nm). If A was adjusted to provide a better fit at longer wavelengths, the approximation would worsen around absorption maxima. This result exposes a limitation of the parametric model and implies the need for further refinement, i.e., its extension for inclusion of additional parameters. Further refinement of the parametric model Eqs.(1)-(3) should consider: (1) extending the functionality of the coefficients A_j for representation of nonlinear influences due to intermolecular interactions between dye molecules and their host environment, which can include different types of dye molecules, as well as those comprising the fiber; and (2) extending the wavelength range of absorption coefficients a_j to include absorption maxima outside the range of interest, which is for proper accounting of off-resonance tails extending into the range of interest. Formally, the coupling of intramolecular absorption modes to intermolecular modes would be included by addition of mixing terms to the function $f(\lambda)$ defined by Eq.(2).

In general, application of the parametric model Eqs.(1) and (2) must consider the inherent statistical nature of diffuse reflectance from a dyed fabric. In particular, agreement between modeled and measured spectra should not be interpreted in the same sense as, for example, thin-film reflectance spectroscopy, where integrated samples are characterized by smooth surface (and thus specular reflection), homogeneous composition, and well-defined thicknesses. In contrast, dyed fabrics are characterized, inherently, by rough surfaces (thus diffuse reflectance), heterogeneous compositions, and nonuniform thicknesses. It follows from the inherent statistical nature of reflection from a dyed fabric that some criterion for relaxed parameter optimization should be applied for modeling spectra. In addition, the parametric model defined by Eqs.(1) and (2) is formulated such that the adjustable parameters A_j account not only for physical processes other than absorption, but also for statistical variations. It follows that the coefficients A_j can be given a statistical interpretation, and thus may be characterized by various types of distributions.

Conclusion

This study examines the diffuse reflectance characteristics of dyed fabrics using a parametric model based on the Beer Lambert law for extinction. The results show good agreement between modeled and experimental reflectance for four NIR/SWIR absorbing dyes in military fabric as a function of concentration and wavelength. The goodness of fits between modeled and experimental reflectance provide validation of the parametric model for simulating the diffuse reflectance of dyed fabrics. These results should contribute to the construction of a parameter space for process optimization of dyed fabrics for SWIR applications. The parameter space in combination with new, automated parameter optimization algorithms would determine the optimal dying process, combinations of dyes, and fabrics needed to obtain a specified dyed fabric spectral response. Future studies should also consider different parametric models for diffuse reflectivity.

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Appendix I

Derivation of Beer-Lambert-Law Parametric Model

The Beer-Lambert-Law parametric model for reflectance defined by Eqs. (1) follows from the Beer Lambert law for transmission based on the first-order differential equation describing the rate of change in downward radiant flux intensity, I_T , within a material, given by

$$\frac{dI_T}{dz} = -\alpha_{ext}(z)I_T \quad (A1)$$

For this system, lateral dimensions of the material are considered infinite, therefore, Eq. (A1) considers energy transport along one dimension. Accordingly, integrating Eq.(A1) over a penetration depth z , i.e.,

$$\int_{I_0}^{I(z)} \frac{dI_T}{I_T} = -\int_0^z \alpha_{ext}(z)dz, \quad (A2)$$

it follows that

$$I_T(z) = I_0 \exp(-\alpha_{ext}z) \quad (A3)$$

Next, it is reasonable to assume that the function $I_T(z)$, which is monotonically decreasing, is essentially zero beyond some average penetration depth $\langle L \rangle$ (see Fig. A1).

At this stage, consistent with the S-matrix formalism of scattering theory [20], it follows that for a system of finite thickness, say $\langle L \rangle$, the transmitted and reflected intensities I_T and R have finite values, and therefore

$$\frac{R}{I_T(z = \langle L \rangle)} = C_{\langle L \rangle} \quad (A4)$$

where the value of $C_{\langle L \rangle}$ depends on the average depth of penetration $\langle L \rangle$. Combining Eq.(A3) and (A4), it follows that

$$R = C_{\langle L \rangle} I_0 \exp(-\alpha_{ext} \langle L \rangle) \quad (A5)$$

Next, letting α_f and α_d represent the extinction coefficients of the undyed fabric and pure dye, respectively, it follows that

$$R_f = I_0 C_{\langle L \rangle} \exp(-\alpha_f \langle L \rangle) \quad (A6)$$

and

$$R_{f+d} = I_0 C_{\langle L \rangle} \exp[-(\alpha_f + \alpha_d) \langle L \rangle] \quad (A7)$$

Finally, dividing Eq.(A7) by Eq.(A6), which is according to background-subtracted reflectance defined by Eq.(5), one obtains Eq.(1) above, where the quantity $\alpha_d \langle L \rangle$, consists, in principle, of an extinction coefficient α_d and an average depth of penetration $\langle L \rangle$. This quantity is expressed by Eq.(2) above, which consists of adjustable parameters A_j and known absorption coefficients $\alpha_j(\lambda)$, for each dye (indexed by j).

Appendix II

Validation of Absorption Coefficients Using Transmission Spectra

One type of validation is provided for the parametric model Eq.(1)-(3) by comparison of predicted transmission spectra, obtained by inversion of dyes in solution, and measured transmission spectra for dyes in fabric, where contributions to the spectra from the fabric are background subtracted. Accordingly, given an absorption coefficient for a pure dye, the predicted transmission spectrum for a dye in fabric, where contributions from the fabric are background subtracted, is given by

$$T_d(\lambda) = C_0 \exp[-\beta\alpha(\lambda)], \quad (\text{A8})$$

where $\beta = Nd$. The quantities N and d are the dye molecule density and effective thickness of the fabric layer. Next, given the assumption that there weak coupling between intramolecular modes, associated with dye-molecule absorption, and intermolecular modes of dye-crystal structures and molecules comprising the fiber, it follows that

$$T_d(\lambda) = \frac{T_{d+f}(\lambda)}{T_f(\lambda)}, \quad (\text{A9})$$

where T_f , T_d and T_{f+d} are the transmittted intensities of the base fabric, pure dye and dyed fabric, and Eq.(A9) specifies a procedure for background subtraction of spectral contributions of the undyed fabric. Comparison of spectra calculated according to Eqs. (A8) and (A9) is by adjustment of the lumped parameters C_0 and β . The parameter C_0 , which is proportional to the incident intensity, is scaled with respect to the background-subtracted transmission spectra Eq.(A9). Accordingly, the values of compared spectral intensities are in arbitrary units. For transmission spectra, the parameter β is well defined with respect to the Beer-Lambert law, and is therefore an ajustable constant. Independent determination of N and d , however, requires additional information. Shown in Fig. (A2) are comparisons of transmission spectra calculated using Eqs. (A8) and (A9).

Tables

Table 1. Optical Dyes under Analysis

Dye Name	Absorption Max (nm)	Solvent
Triarylamine	978	Acetone
Tetraaryldiamine	949	Acetone
Metal Dithiolene	836	Methylene Chloride
Indolium Iodide	775	Methanol

Figures

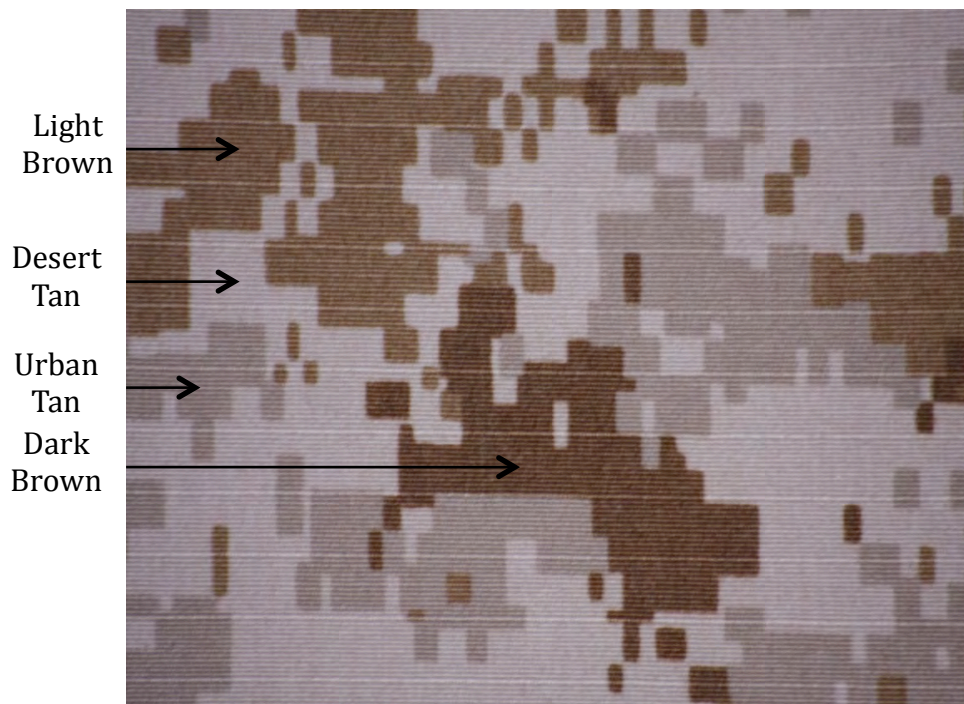


Figure 1. Macroscopic sample of base fabric considered for dye application, 50% Nylon, 50% Cotton blend Ripstop fabric, i.e. 50/50 NYCO Ripstop.

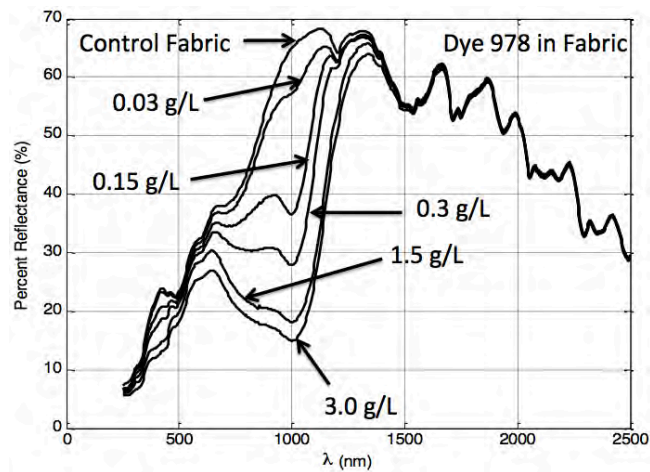


Figure 2. Experimentally measured reflectance spectra for fabric with and without Triarylamine dye as a function of dye concentration.

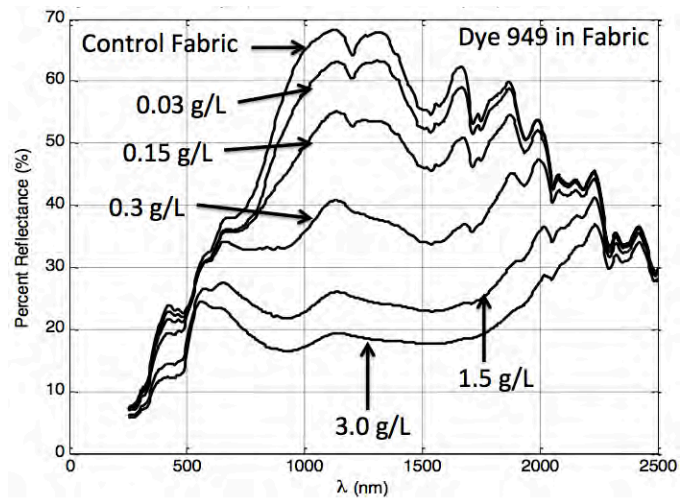


Figure 3. Experimentally measured reflectance spectra for fabric with and without Tetraaryldiamine dye embedded as a function of dye concentration.

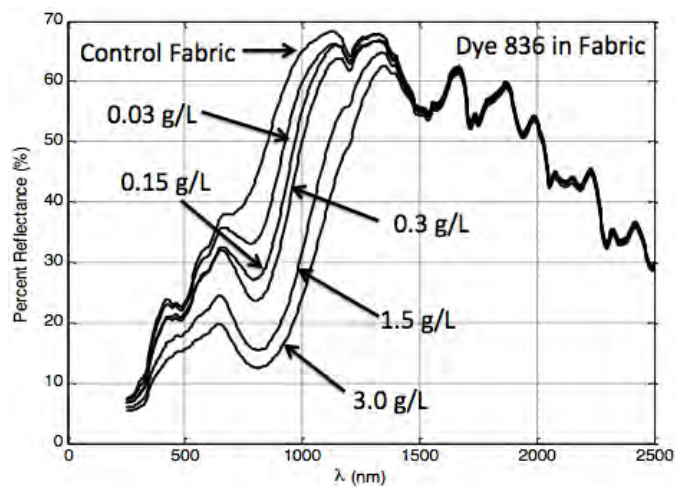


Figure 4. Experimentally measured reflectance spectra for fabric with and without Transition Metal Dithiolene dye embedded as a function of dye concentration.

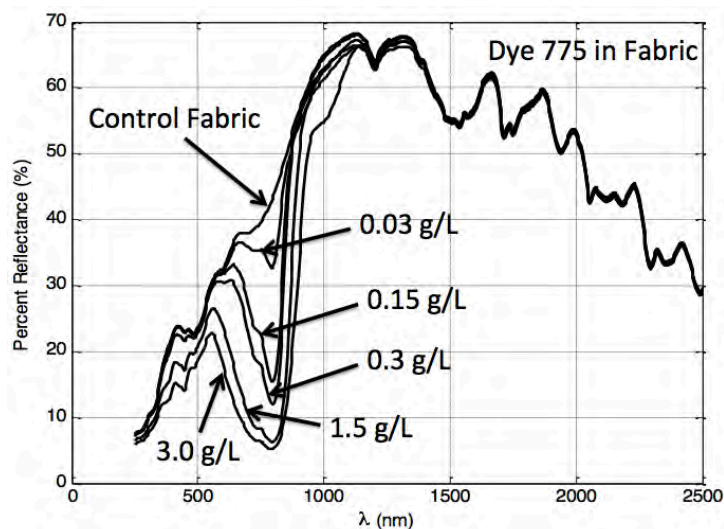
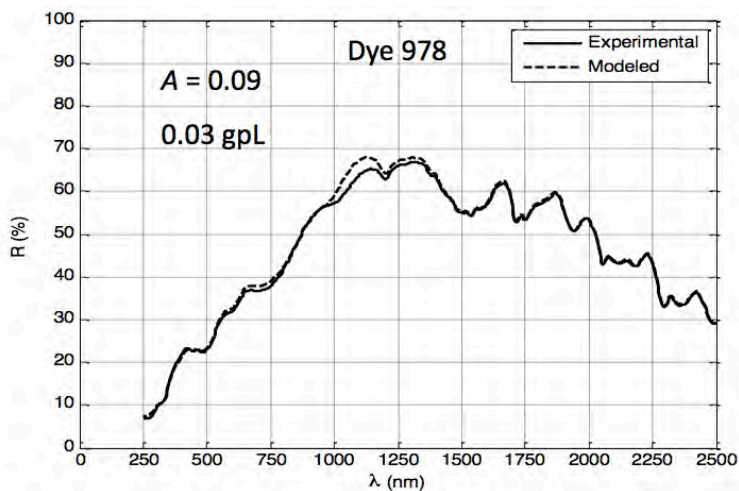
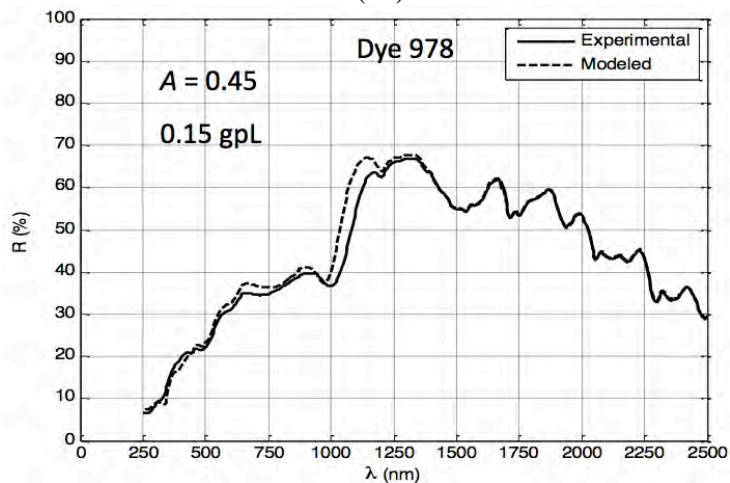


Figure 5. Experimentally measured reflectance spectra for fabric with and without Indolium Iodide dye embedded as a function of dye concentration.



(6a)



(6b)

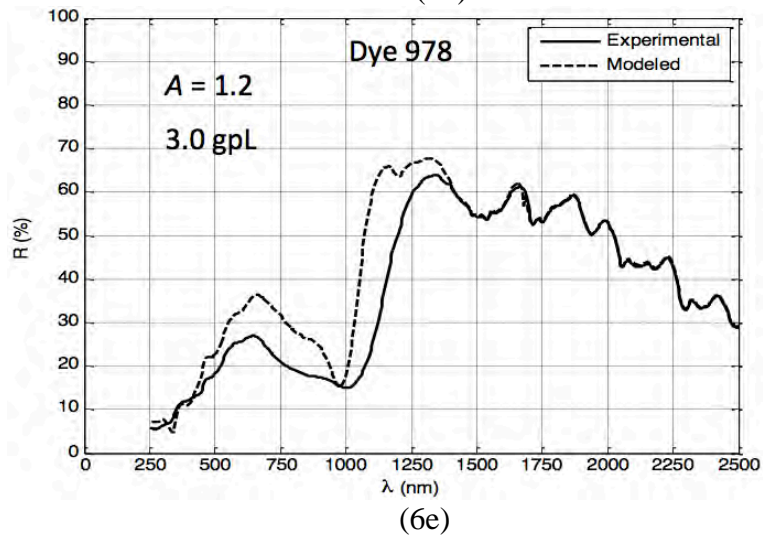
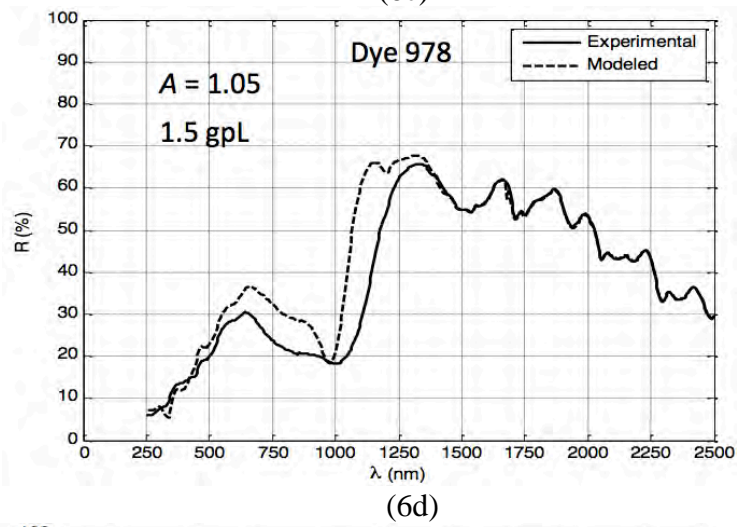
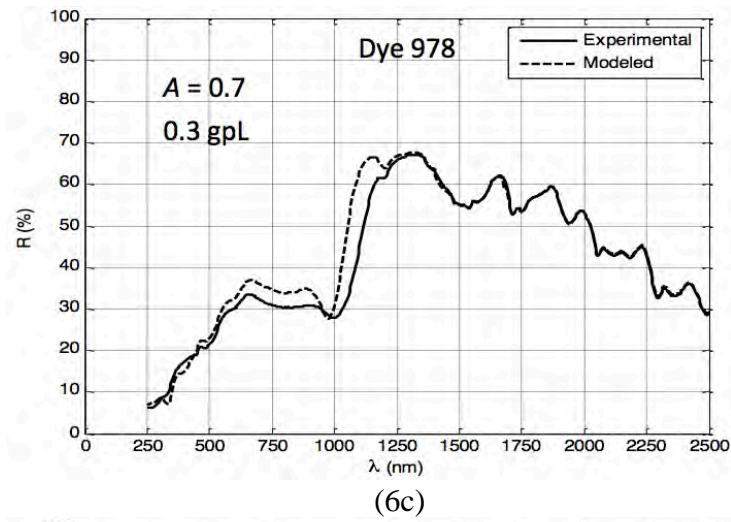
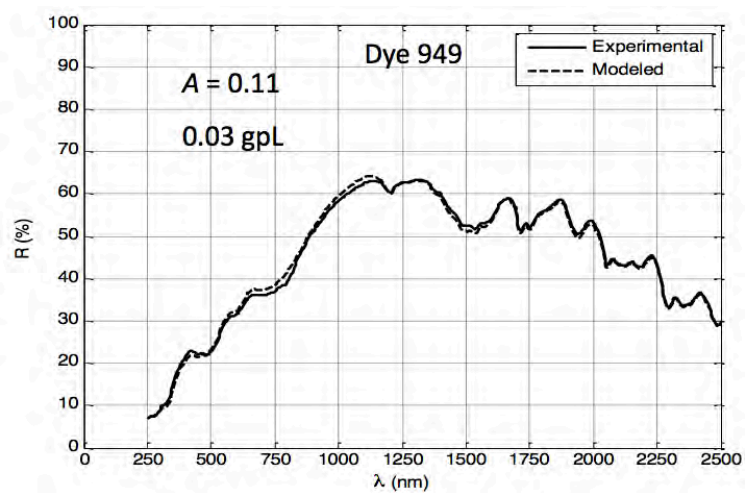
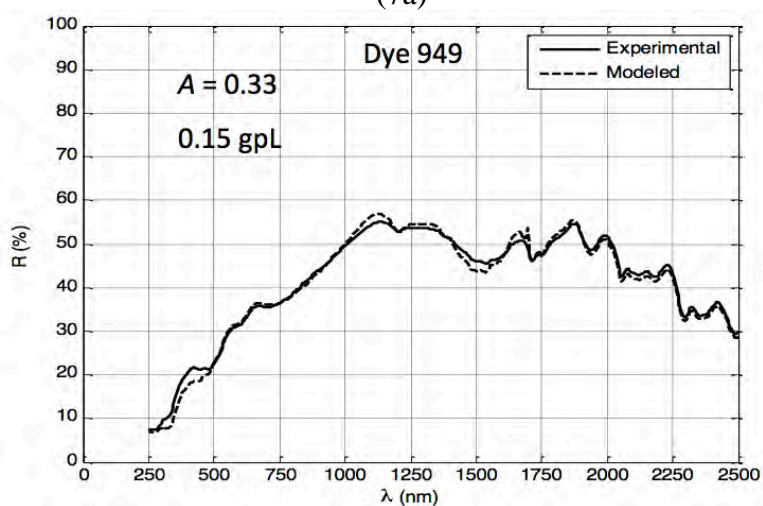


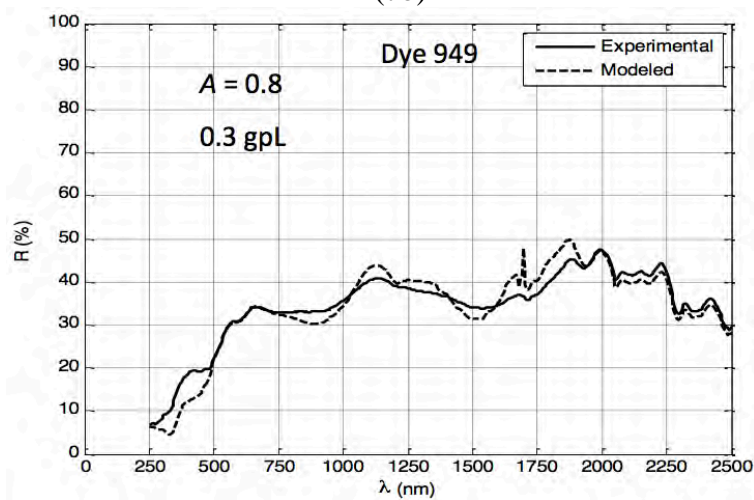
Figure 6. Modeled and measured reflectance spectra for fabrics dyed with different concentrations of Triarylamine dye in solution.



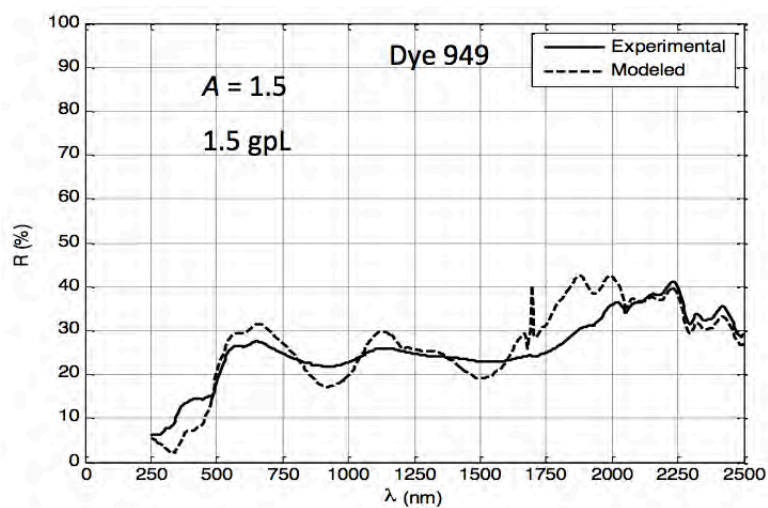
(7a)



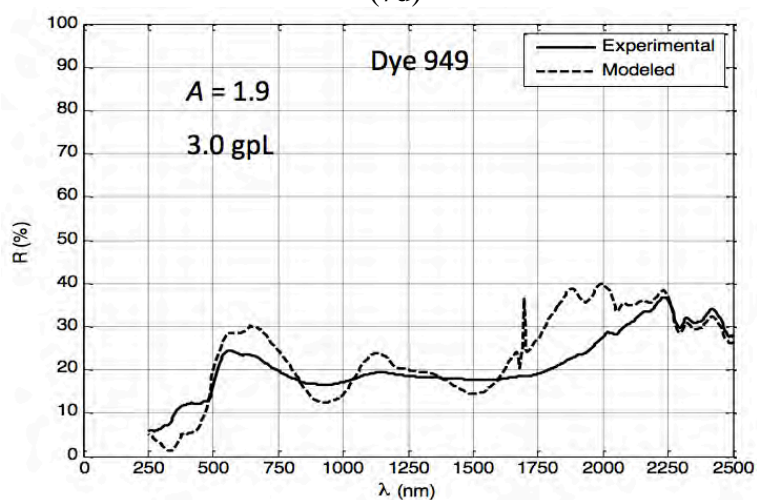
(7b)



(7c)

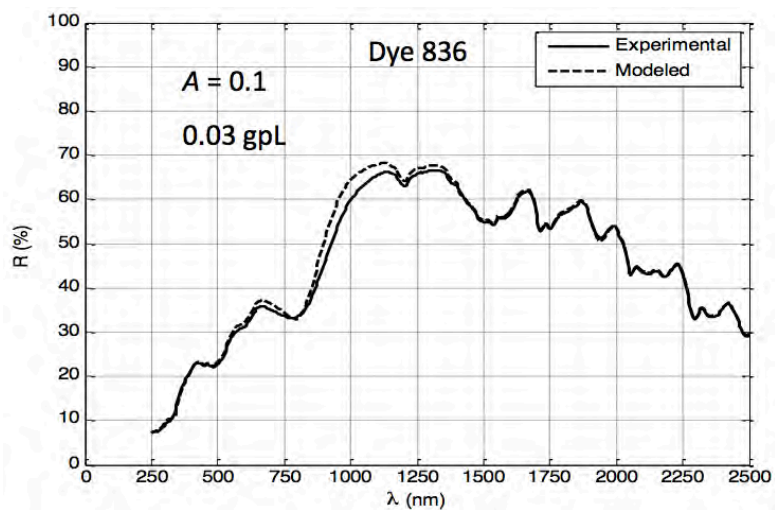


(7d)

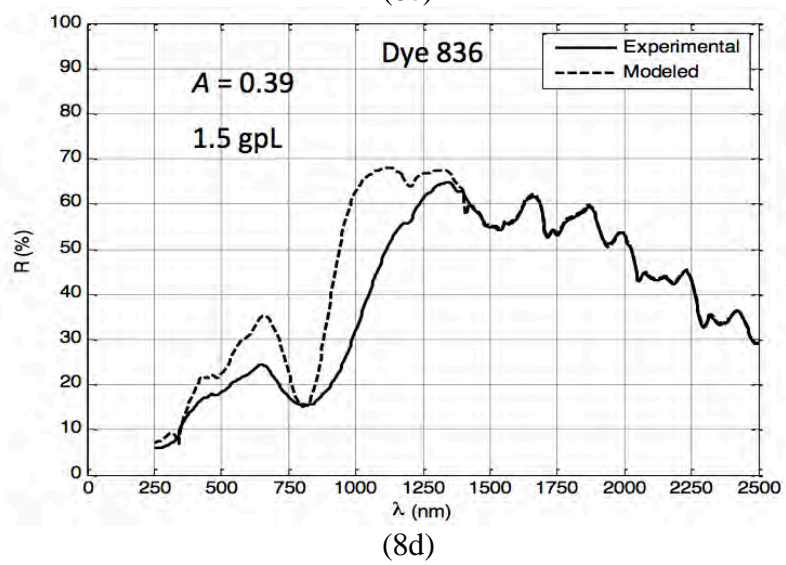
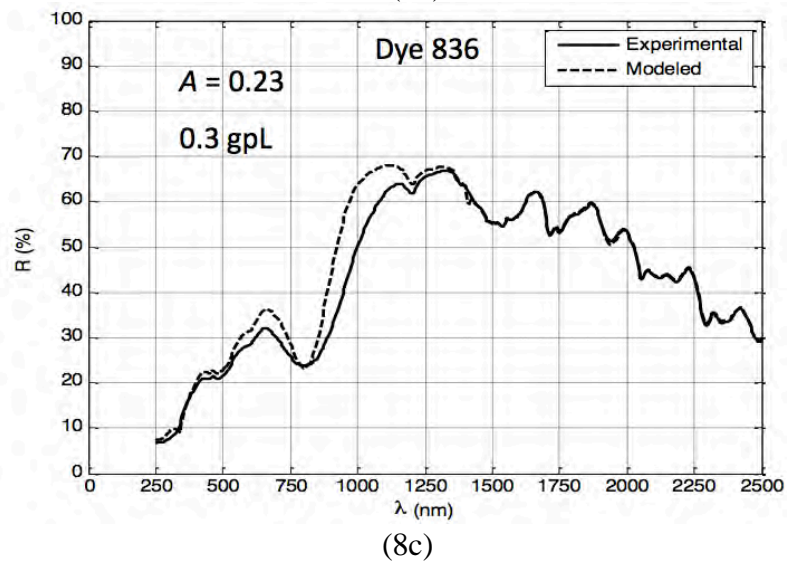
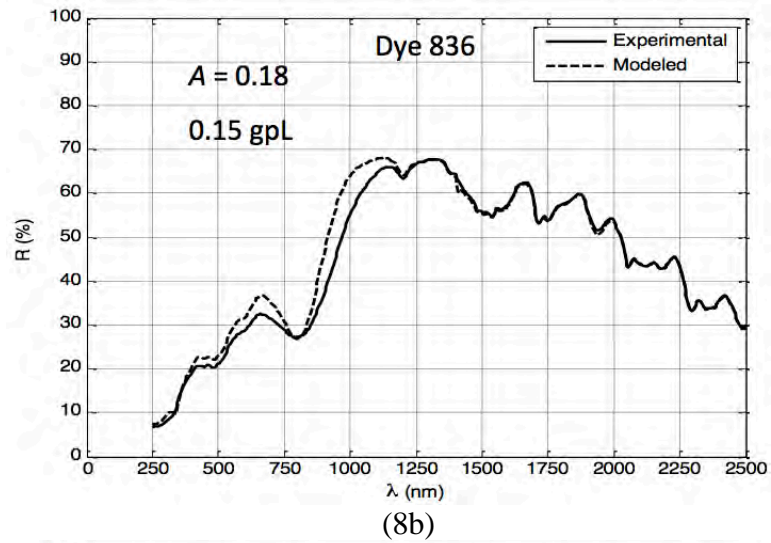


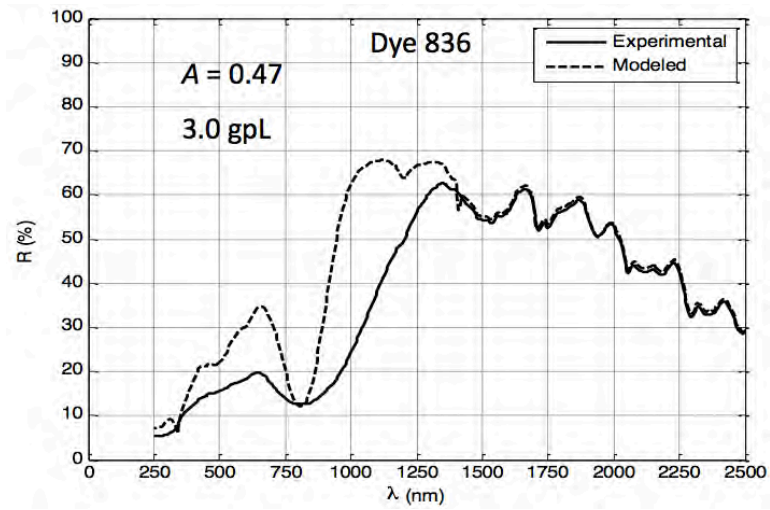
(7e)

Figure 7. Modeled and measured reflectance spectra for fabrics dyed with different concentrations of Tetraaryldiamine dye in solution.



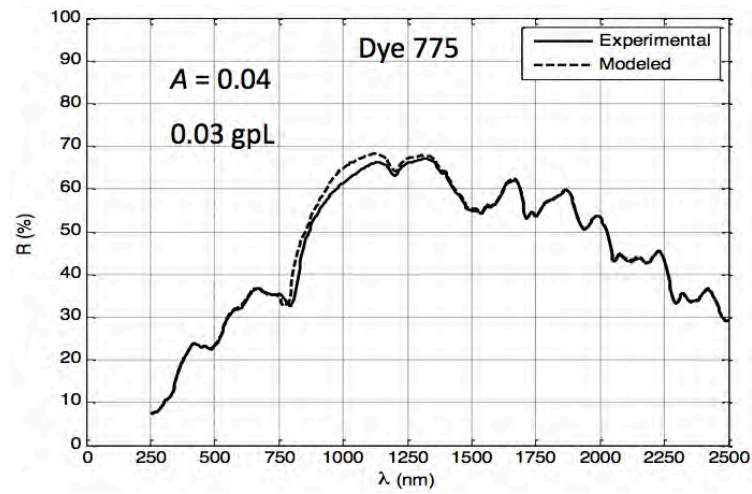
(8a)



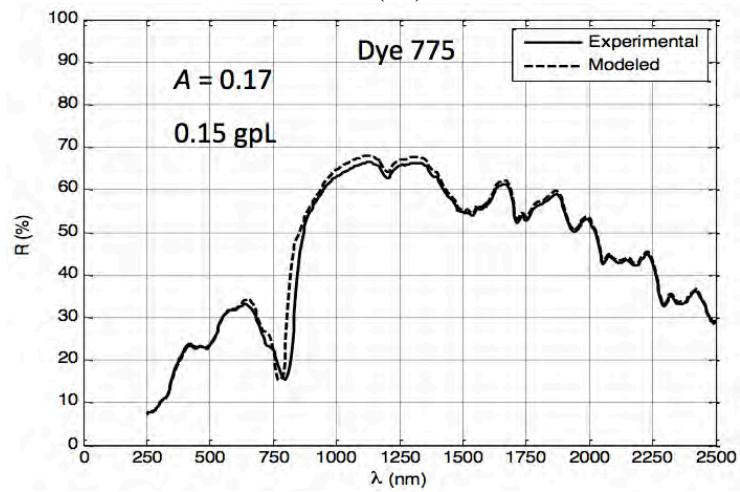


(8e)

Figure 8. Modeled and measured reflectance spectra for fabrics dyed with different concentrations of Transition Metal Dithiolene dye in solution.



(9a)



(9b)

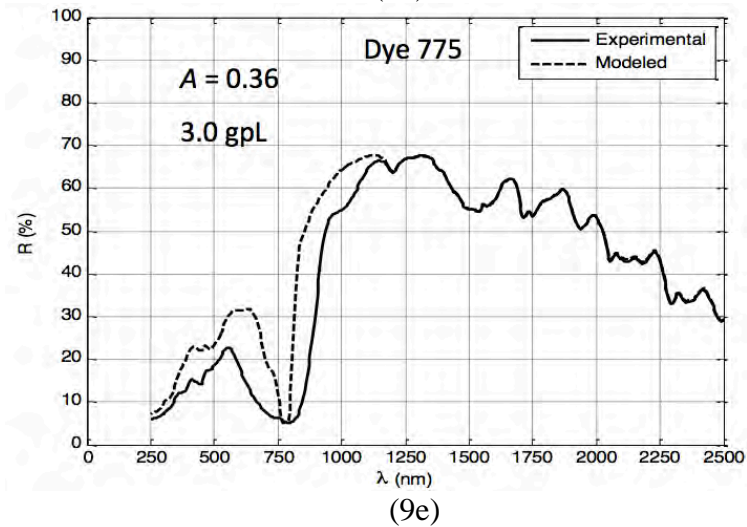
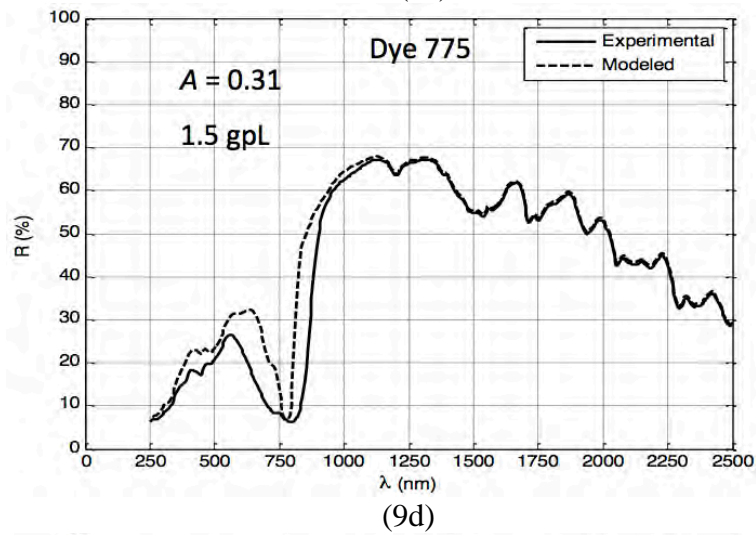
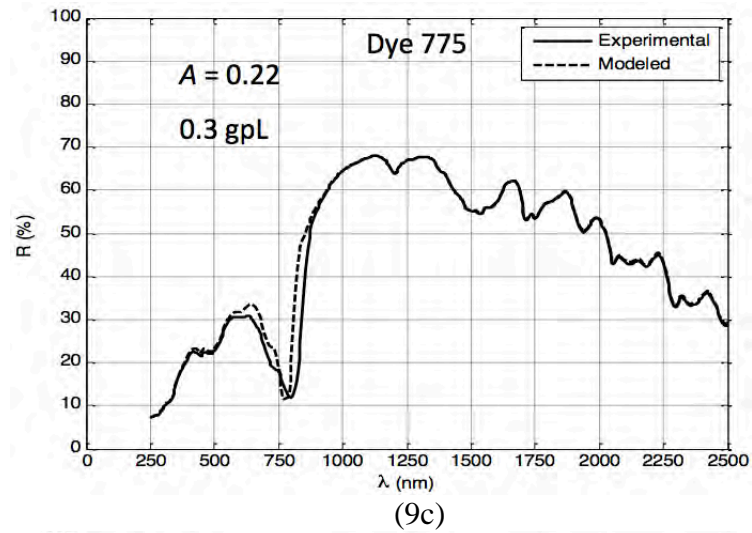


Figure 9. Modeled and measured reflectance spectra for fabrics dyed with different concentrations of Indolium Iodide dye in solution.

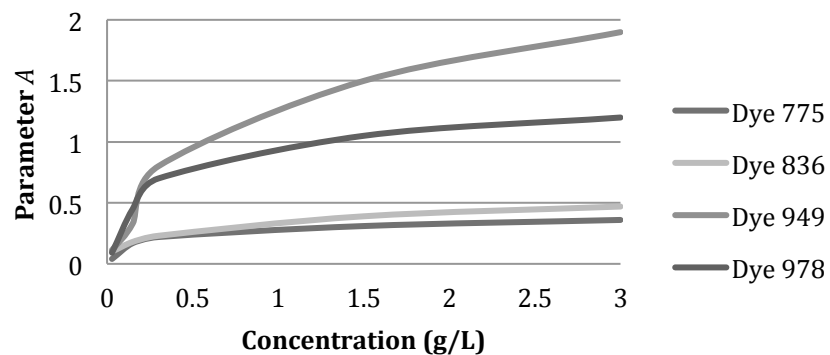
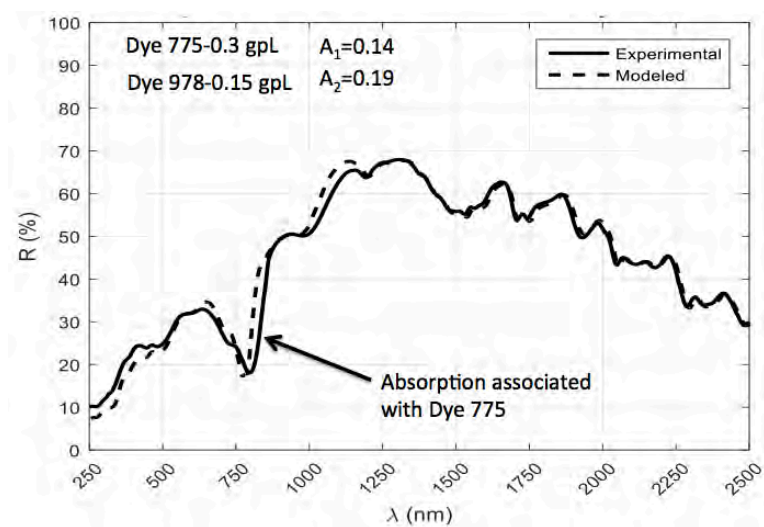
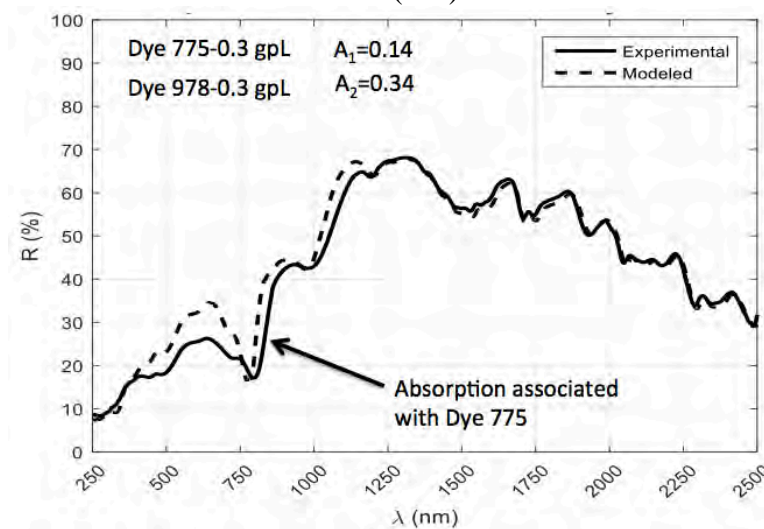


Figure 10. Parameter A as a function of dye type and concentration.



(11a)



(11b)

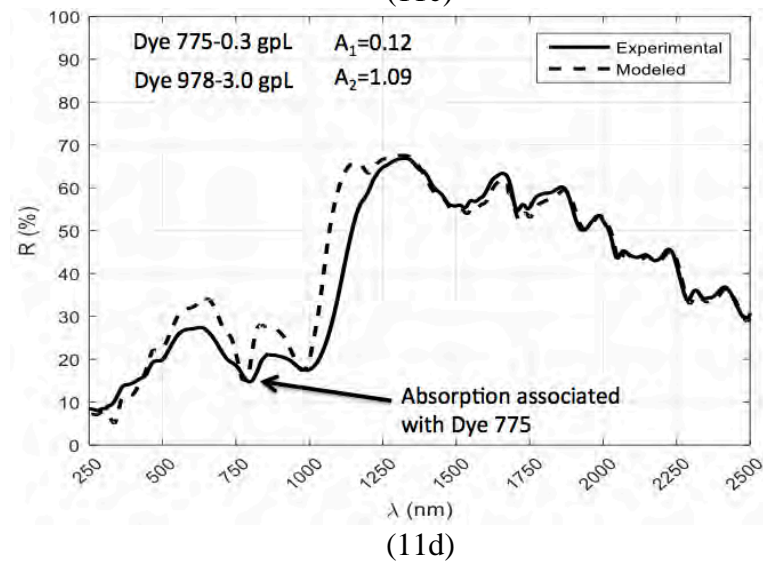
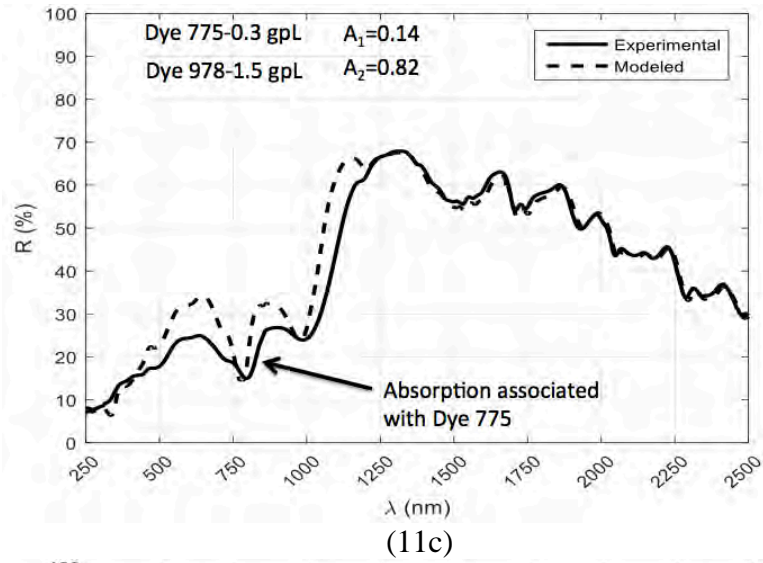
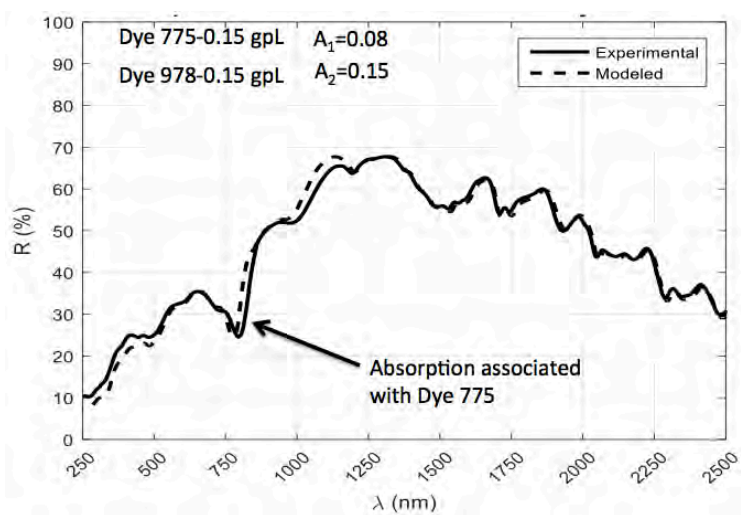
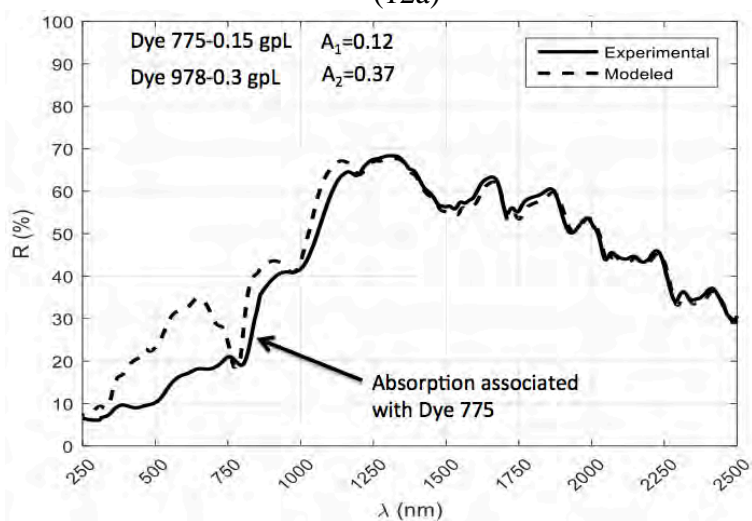


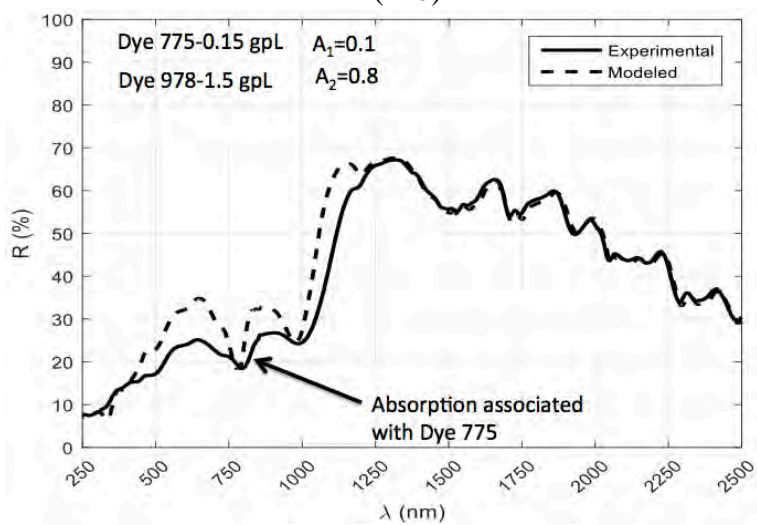
Figure 11. Modeled and measured reflectance spectra for fabrics dyed with different relative concentrations of Triarylamine and Indolium Iodide dyes in solution. Indolium Iodide dye concentration in solution fixed at 0.3 gpL.



(12a)



(12b)



(12c)

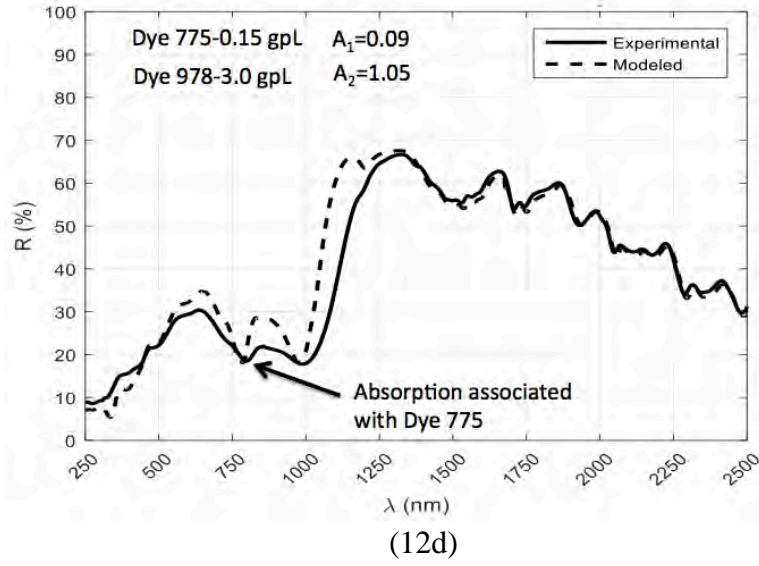


Figure 12. Modeled and measured reflectance spectra for fabrics dyed with different relative concentrations of Triarylamine and Indolium Iodide dyes in solution. Indolium Iodide dye concentration in solution fixed at 0.15 g/L.

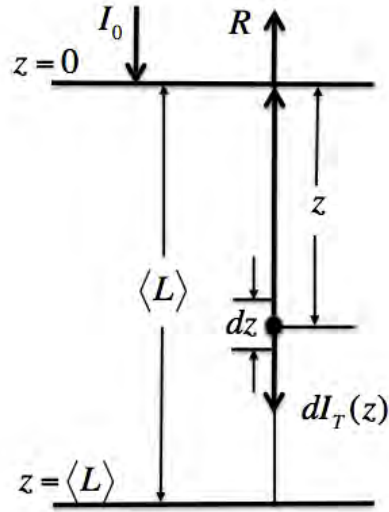
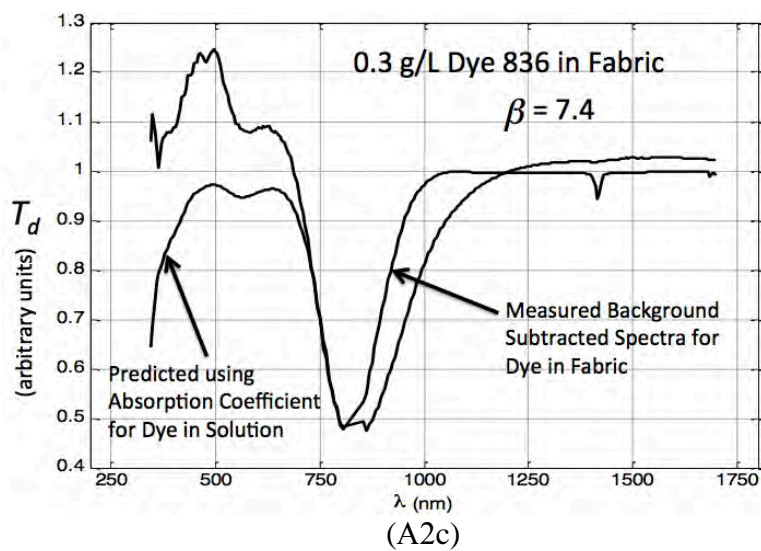
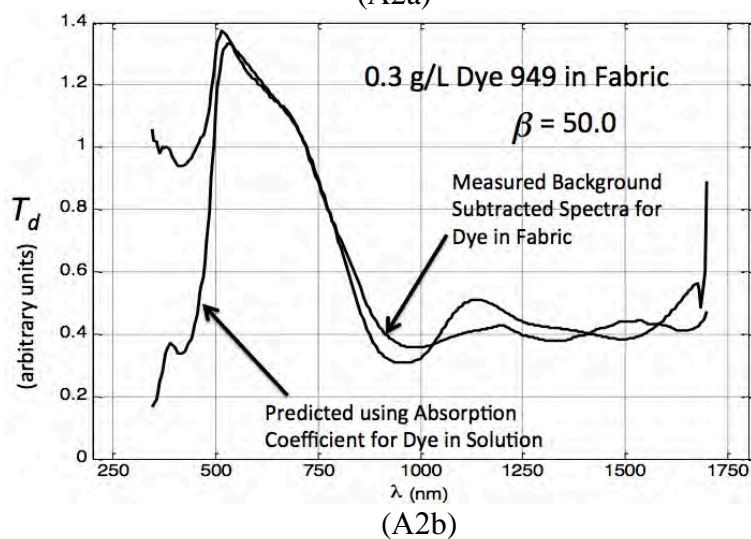
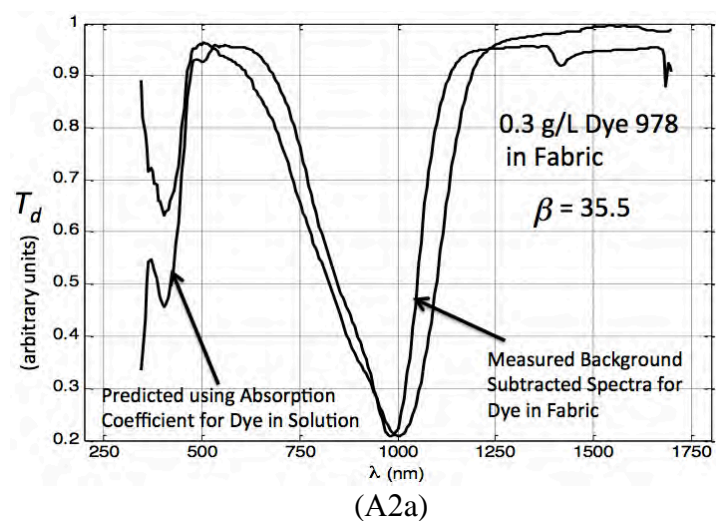


Figure A1. Schematic representation of quantities comprising Eqs. (A1) through (A7).



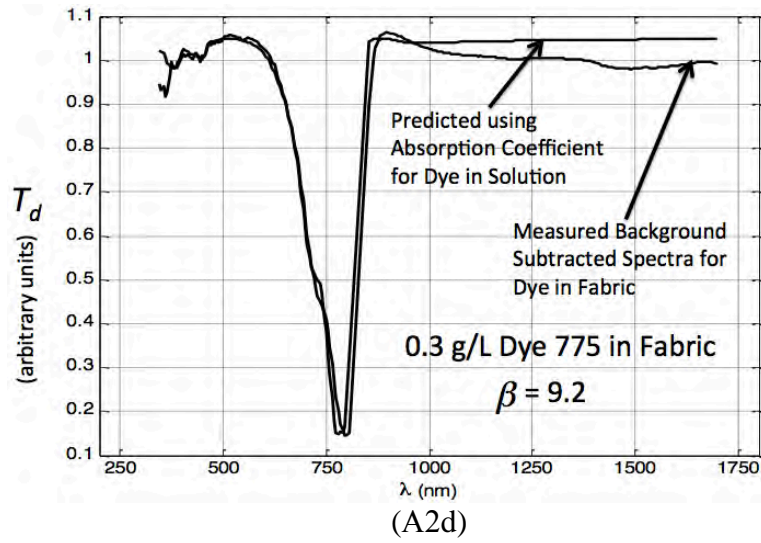


Figure A2. Comparisons of modeled and measured transmission spectra calculated using Eqs. (A8) and (A9), respectively.

